

# PHASE EVOLUTION DURING CONVENTIONAL AND FLASH SINTERING OF HYDROXYAPATITE-ZIRCONIA COMPOSITE USING *IN-SITU* SYNCHROTRON X-RAY DIFFRACTION

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Flash Sintering (FS) is a technique capable of sintering ceramics in a few seconds and at lower furnace temperatures than the conventional sintering (CS) technique. Despite this clear advantage of reducing the processing temperature and times, the mechanisms behind such remarkable sintering method are still unclear. The main question yet to be addressed is: *how important is the role of athermal effects promoted by the electric field in this sintering process?* To bring some light to this subject, in this work we compared the thermal history, crystalline phase evolution, and microstructure of hydroxyapatite-zirconia (Hap-3YSZ) composite prepared by both FS and CS.

For that, wet chemically prepared HAp (50%wt.) powders were mixed with commercial 3YSZ (50%wt.) powders in a vibratory mill. Then, the samples were shaped using uniaxial pressing (280 MPa) into rectangular bars with a cross-section of 1.5 mm x 3.5 mm and a length of 4.4 mm. To evaluate phase evolution, *in-situ* synchrotron X-ray diffraction (XRD) was performed at the National Synchrotron Light Source – II at Brookhaven National Laboratory. A thin layer of platinum paste was painted on the sample surface to calculate its temperature using Pt thermal expansion. A quadrupole lamp furnace was used to heat the samples, and a full diffraction pattern was obtained every second. Isothermal FS was performed at 1000 °C with a DC electric field of 500 V cm<sup>-1</sup> and a current density limit of 20 mA mm<sup>-2</sup> (held for 10 s). CS was carried out at 1400 °C (30 °C min<sup>-1</sup>) for 10 min. Rietveld refinement was used to determine and quantify the phase evolution of the samples. Finally, the samples' fractured surfaces were analyzed by scanning electron microscopy (SEM).

The maximum temperatures calculated using the Pt-Standard method during the CS and the FS experiments were, respectively, 1400 °C (with heating rate of 30 °C min<sup>-1</sup>) and 1370 °C (with heating rate of 104 °C min<sup>-1</sup> from 1000 to 1370 °C). Regarding phase evolution, the starting HAp and 3YSZ tetragonal phases were kept as the major structures during CS. However, during FS the HAp was completely transformed into  $\alpha$ -tricalcium phosphate ( $\alpha$ -TCP) and the tetragonal 3YSZ transformed into a cubic phase. These phase transformations occurred at the moment when the electric current increased abruptly (flash event). The results indicate that calcium ions migrate from the HAp structure, co-doping 3YSZ and stabilizing its cubic phase at room temperature. The Rietveld refinement corroborates this hypothesis since a better fit was obtained when using a co-doping fraction of 3 mol% yttrium and 6 mol% calcium. SEM images of the fractured surfaces of both CSed and FSed samples are presented in Figure 1. Needle-shaped microstructures were formed in the FSed samples. In contrast, these microstructures were not observed in the CSed counterpart. The needle-like microstructure formation is consistent with a vapor-liquid-solid (VLS) mechanism, i.e., the formation of materials' liquid and vapor phases, followed by electric field-driven recrystallization. The electrical parameters of FS combined with the characteristics of HAp ionic conduction mechanisms may be responsible for the activation of the VLS mechanism in the material, causing the formation of these unique dandelion-like crystals.

We show that CSed and FSed Hap-3YSZ composites that reached similar maximum temperatures present substantial differences in both microstructure and phase evolution. The results suggest that athermal effects of

the electric field (applied during FS) can play an important role during sintering of this composite by activating the VLS re-crystallization mechanism. It is noteworthy that the different heating rates between the experiments could also contribute to the CS and FS distinct results. Therefore, further comparison of FS with other fast-firing processes with similar heating rates and without an electric field would be interesting (e.g., laser sintering, ultra-fast high temperature sintering).

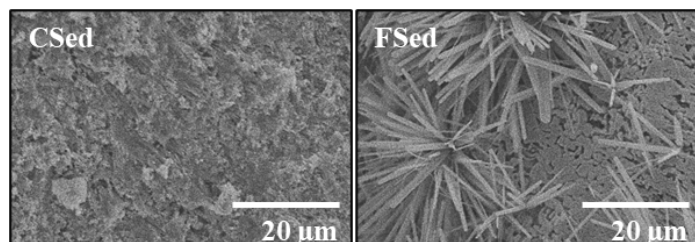


Figure 1 – Fractured surfaces microstructures of CSed and FSed Hap-3YSZ composites.